JP 2002-179600 A

(11)Publication number : 2002-179600
(43)Date of publication of application : 26.06.2002
(51)Int.CI. C07C 29/62
C07C 29/80
C07C 29/86
C07C 31/36
// C07B 61/00

(21)Application number : 2000-379783
(22)Date of filing : 08.12.2000

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(54) METHOD FOR PRODUCING HIGH-PURITY 3-CHLORO-1-PROPANOL

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for easily, industrially and efficiently producing high-purity 3-chloro-1-propanol free from impurities including its ether modification by selectively chlorinating 1,3-propanediol with hydrochloric acid or a hydrogen chloride gas as the hydrogen chloride source.
SOLUTION: This method for producing high-purity 3-chloro-1-propanol comprises the steps of reacting a hydrogen chloride source with 1,3-propanediol at 50-100[deg]C to obtain a reaction liquid containing 3-chloro-1-propanol and then extracting and removing impurities present in the reaction liquid with a hydrophobic organic solvent.

CLAIMS

[Claim(s)]

[Claim 1]The manufacture approach of the high grade 3-chloro-1-propanol characterized by carrying out extract clearance of the impurity which obtains the reaction mixture which the source of a hydrogen chloride is made to react to 1,3-propanediol at 60-100 degrees C, and contains 3-chloro-1-propanol, and exists subsequently to the inside of said reaction mixture with a hydrophobic organic solvent.

[Claim 2]The manufacture approach of the high grade 3-chloro-1-propanol according to claim 1 characterized by distilling after carrying out extract clearance.

[Claim 3]The manufacture approach of the high grade 3-chloro-1-propanol according to claim 1 or 2 characterized by being one sort chosen from the group which a hydrophobic organic solvent becomes from hydrocarbons, halogenated hydrocarbon, ester, ether, ketones, carbonate, and olefins, or two sorts or more.

[Claim 4]The manufacture approach of the high grade 3-chloro-1-propanol according to claim 1 to 3 characterized by making the source of a hydrogen chloride react to 1,3-propanediol under existence of a catalyst.

[Claim 5]The approach according to claim 4 of being one sort chosen from the group which a catalyst becomes from zeolites, halogen metal salts, quarternary ammonium salt, and phosphonium salt, or two sorts or more.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the approach of being a high grade from 1,3-propanediol, and manufacturing 3-chloro-1-propanol by high yield. High grade 3-chloro-1-propanol is an important compound industrially as useful raw materials, such as a remedy, agricultural chemicals, and a polymer.

[0002]

[Description of the Prior Art]Conventionally, as the manufacture approach of 3-chloro-1-propanol, the process (JP,52-42769,B) by the ester exchange reaction (the West German country patent application official report No. 2436602 description) of 1 and 3-chloropropyl acetate and the reduction reaction following hydrochloric-acid addition and it of an acrolein is known. However, each of these approaches was two staircase reactions, and especially the latter had the point using sodium borohydride expensive as reduction materials etc. to the high manufacturing cost, and they had become the constraint on industrial utilization.

[0003]on the other hand, since it is old, the method (C. S.Marvel et al., ORUGA nick SHINSHI seeds (Organic Syntheses), Coll.Vol.I, 533-535page (1964)) of making a hydrochloric acid or hydrogen chloride gas react to 1,3-propanediol, and manufacturing 3-chloro-1-propanol is learned as the simple manufacture approach of 3-chloro-1-propanol. However, this approach was a reaction under a 150-170-degree C elevated temperature, by high invert ratio manufacture, selectivity fell and, as for these impurities, the chlorohydrin obtained had the problem that clearance was difficult, by distillation including impurity ether objects, such as 1 and 3-dichloropropane and the bis(3-chloropropyl) ether. When distillation purification of the 3-chloro-1-propanol including many these ether objects is carried out, the yield of the 3-chloro-1-propanol made into the object decreases extremely, and a high grade product is not obtained. moreover -- the time of a low invert ratio -- 1 and 3-dichloropropane -- and although the amount

of generation of that impurity ether object can be reduced by how many sorts, yield is low and unsuitable as a industrial process from a cost side.

[0004]Thus, the manufacture approach that high grade 3-chloro-1-propanol could be industrially obtained by high yield simple was searched for.

[0005]
[Problem(s) to be Solved by the Invention]The object of this invention is to offer the approach of manufacturing industrially efficiently the high grade 3-chloro-1-propanol which does not contain impurities, such as an ether object, simple, when it chlorinates selectively from 1,3-propanediol in view of the above-mentioned technical problem, using a hydrochloric acid and hydrogen chloride gas as a source of a hydrogen chloride.
[0006]
[Means for Solving the Problem]The result of having examined wholeheartedly how for this invention person etc. to chlorinate 1,3-propanediol selectively, and to obtain high grade 3-chloro-1-propanol, If it chlorinates in the range with a reaction temperature of 60-100 degrees C under existence of a specific catalyst or un-existing by the hydrochloric acid and hydrogen chloride gas which are a source of a hydrogen chlorideBy obtaining 3-chloro-1-propanol with sufficient selectivity, then washing reaction mixture using hydrophobic organic solvents, such as toluene and a pentaneImpurities, such as an ether object, are easily removable to a surprising thing. Consequently, the manufacture approach of the simple high grade 3-chloro-1-propanol that the high grade 3-chloro-1-propanol made into the object very efficiently by distillation can be obtained is found out, and it came to complete this invention at last.
[0007]This invention is explained below at a detail.
[0008]Although a hydrochloric acid and hydrogen chloride gas are mentioned and these can be respectively used independently as a source of a hydrogen chloride used for this invention, it can also use together and use.
[0009]In that case, as an amount of the hydrogen chloride usually used, it is desirable to use more than a 1 time mol to the 1,3-propanediol which is a start compound in order to make an invert ratio high, and in order to raise the selectivity of a reaction further, the activity of a 1.1 to 1.5 time mol is still more desirable. On the other hand, the ether object with which 1 which carries out a byproduction, 3-dichloropropane, and its clearance are difficult, and pose a problem may increase the activity of the hydrogen chloride of the amount exceeding a mol 1.5 times.
[0010]Moreover, if the entrainment rate in the case of using hydrogen chloride gas is an entrainment rate generally used on a industrial scale (for example, the range of 5 - 200 kg/m3 and hr), it will not influence generation of impurities, such as a by-product.
[0011]The range of reaction temperature of the point of the selectivity of a rate of reaction and 1,3-propanediol to 60-100 degrees C is desirable. On the intense heating conditions which a reaction cannot progress easily at the low temperature of less than 60 degrees C in reaction temperature, and exceed 100 degrees C, the amount of generation of 1 and 3-dichloropropane and an ether object increases, and since the selectivity of 3-chloro-1-propanol falls remarkably, it is not desirable.
[0012]In the approach of this invention, even if it does not use a catalyst for a reaction, a reaction can fully be advanced. Furthermore, by carrying out under existence of a catalyst in the case of a reaction, also at comparatively low temperature, a reaction can be advanced and improvement in a reaction rate and selectivity is accepted.
[0013]When making it react under existence of a catalyst, as a catalyst used, Lewis acid, such as a halogen metal chloride of beta mold acidity zeolite, the zeolites of H-ZSM5 grade, $FeCl_3$, and $ZnCl_2$ grade, is mentioned, for example. Besides these, a tetrabutylammonium star's picture, tetrabuthyl ammoniumchloride, Tetrabutylammonium iodide, tetrabutylammonium hydroxide, a tetrabutylammonium

flora -- the id and a tetrabutylammonium flora -- the id -- a hydrate --A tetrabutylammonium ape fight, a tetrabutylammonium hydrogen ape fight, A benzyl trimethylammonium chloride and benzyl trimethylammonium chloride mono-hydrate, a benzyl trimethylammonium star's picture and a benzyl trimethylammonium flora -- the id - hydrate --Benzyl trimethylammonium hydroxide, a benzyl trimethylammonium METOKI side, Quarternary ammonium salt, such as a tetra-octadecyl ammonium star's picture, a tetra-octyl ammonium star's picture, and tetra-octyl ammonium FURORAIDO, and phosphonium salt, such as a tetra-octyl phosphonium star's picture, can be used as a catalyst. Although these catalysts can be used by the one-sort independent, it does not interfere, even if it uses combining two or more sorts.

[0014]As an amount of the catalyst used, 0.1 - 10% of the weight of the range is desirable at weight % to the 1,3-propanediol which is a start compound, and 1 - 5% of the weight of the range is still more desirable.

[0015]In the approach of this invention, a hydrophobic organic solvent is added by reaction mixture after a chlorination reaction, and extract clearance of the impurity in reaction mixture is carried out at this hydrophobic organic solvent. A hydrophobic organic solvent can be added to reaction mixture, and a well-known approach and equipment can be used for extracting.

[0016]As a hydrophobic organic solvent used, it is hydrophobicity, and the 3-chloro-1-propanol which carried out water is not not much dissolved, and the solvent which melts the ether object of an impurity and 1 and 3-dichloropropane well is chosen.

[0017]If such a hydrophobic organic solvent is mentioned still more concretely, a pentane, a hexane, A heptane, an octane, a nonane, Deccan, an undecane, a dodecane, a tridecane, the shape of a straight chain, such as tetradecane, pentadecane, hexadecane, heptadecane, and an OKUTA decane, -- and2-methyl butane, 2-methyl pentane, 3-methyl pentane, 2-methyl hexane, 3-methyl hexane, 2-methylheptane, 2, and 2-dimethyl hexane, Chain-like aliphatic hydrocarbon with side chains, such as 2 and 3-dimethyl heptane; A cyclohexane, Cyclic hydrocarbons, such as a methylcyclohexane; Benzene, toluene, o-, m-, para xylene, Aromatic hydrocarbon, such as ethylbenzene; Dichloromethane, chloroform, A carbon tetrachloride, a dichloroethane, chloropropane, 1, 3-dichloropropane, 1,2-dichloropropane, n-butyl chloride, 1, 4-dichlorobutane, 1, 3-dichlorobutane, n-pentyl chloride, cyclopentyl chloride, n-hexyl chloride, cyclohexyl chloride, n-octyl chloride, n-lauryl chloride, dibromomethane, bromoform, tetrabromo methane, n-propyl star's picture, i-propyl star's picture, 1,3-dibromopropane, 1, 2-dibromopropane, n-butyl star's picture, 1,4-dibromobutane, 1, 3-dibromo butane, n-pentyl star's picture, a cyclopentyl star's picture, n-hexyl star's picture, a cyclohexyl star's picture, n-octyl star's picture, Aliphatic series halogenated compounds, such as n-lauryl star's picture; A chlorobenzene, o-, m-, p-dichlorobenzene, o-, m-, p-chloro toluene, Aromatic series halogenated compounds, such as o-, m-, p-BUROMO toluene, alpha and alpha, and benzotrifluoride; Methyl acetate, Aliphatic series ester, such as ethyl acetate, isopropyl acetate, butyl acetate, and isobutyl acetate; Methyl benzoate, Aromatic series ester, such as ethyl benzoate and benzoic-acid isobutyl; Diethylether, Diisopropyl ether, methyl t-butyl ether, the JIISO aluminum ether, Aliphatic series ether, such as chloromethyl methyl ether and bromomethyl methyl ether; An anisole, Aromatic series ether, such as a phenetole, diphenyl ether, and trifluoro methoxybenzene; A methyl ethyl ketone, Carbonate, such as aromatic ketone; diethyl carbonate, such as methyl isobutyl ketone, a cyclohexanone, and 3-methyl pen TENON, and JI t-butyl carbonate; olefins, such as a cyclohexene, are mentioned. Chain-like aliphatic hydrocarbon, aromatic hydrocarbon, and aliphatic series halogenated compounds are [especially among these] desirable. Moreover, although these hydrophobic organic solvents can be used independently respectively, two or more can also be used together and used for them.

[0018]In addition, if there is 5 % of the weight or more of amounts of the hydrophobic organic solvent used for an extract to reaction mixture, they are

enough. On the other hand, if washing clearance is carried out using the amount of solvents in which this amount exceeds 50 % of the weight, extract clearance also of the 3-chloro-1-propanol made into the object other than an impurity is carried out, and that yield may fall. Therefore, 5 % of the weight - 50% of the weight of an activity is more desirable. Moreover, although 1 time is sufficient as the count of an extract, it is repeatedly good in a line at a little solvent.

[0019]Although a hydrophobic organic solvent is added to reaction mixture as mentioned above and an impurity is extracted as an organic solvent phase, the organic solvent phase in which this impurity is contained is removed by separation means, such as liquid separation. What is necessary is for the approach and equipment which are usually used just to also perform the clearance approach.

[0020]The phase containing the 3-chloro-1-propanol from which the impurity was removed is fully a high grade, even when it remains as it is, but in order that it may raise purity further, can distill this and can take up high grade 3-chloro-1-propanol. By the approach and equipment which are usually used, although the conditions of distillation do not generally have **********, they are usually performed on reduced pressure conditions, and a distillation temperature just attains the object of this invention.

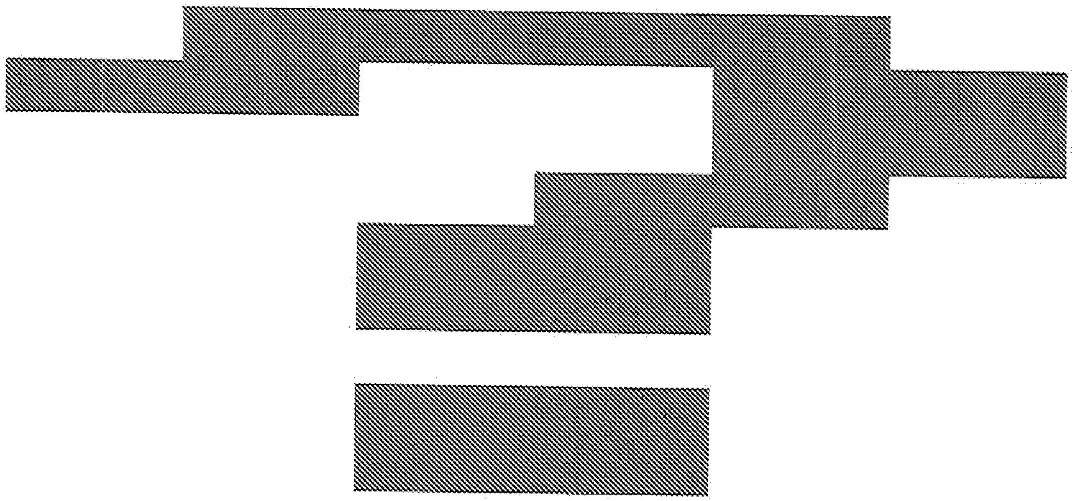
[0021]

[Example]Although an example explains the detail of a reaction below, they do not limit this invention. In addition, the product of this reaction was checked in GC-MS. Moreover, each analyzed and checked yield using the gas chromatography.

[0022]An example 11, 3-propanediol 38.1g (0.50 mols) and H-ZSM5 It attaches to an oil bath, and agitating, hydrogen chloride gas 24g (0.65 mols) was blown, and was made to put 0.78g (2.0 % of the weight) into the 4 opening flask equipped with a reflux capacitor, a thermometer, and a magnetic churning child, and to react over 17 hours with the internal temperature of 80 degrees C. Consequently, the 3-chloro-1-propanol which 57.2g of water reaction mixture is obtained, and the invert ratio of 1,3-propanediol makes the object 92.6% was 34.2g (0.36 mols) and 72.4% of yield. Moreover, the content of 1 which carried out the byproduction, 3-dichloropropane, and the bis(3-chloropropyl) ether was 9.3% and 1.8% respectively. Subsequently, toluene 20.0g (40 % of the weight) was added using 50.0g of the water reaction mixture, and the organic layer including the ether object of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether which were put and carried out the byproduction after liquid separation was removed after churning. Consequently, the content of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether became 1.0% and 0.3% respectively. The presentation after the yield in each process, the invert ratio of a raw material, the selectivity of a reaction, and processing at each process (the rate of the area by GC measurement shows) is shown in a table 1.

[0023]

[A table 1]



[0024]An example 21, 3-propanediol 38.1g (0.5 mols) and FeCl3 It attaches to an oil bath, and agitating, hydrogen chloride gas 24g (0.65 mols) was blown, and was made to put 0.78g (2.0 % of the weight) into the 4 opening flask equipped with a reflux capacitor, a thermometer, and a magnetic churning child, and to react over 11 hours with the internal temperature of 95 degrees C. Consequently, the 3-chloro-1-propanol which 58.7g of water reaction mixture is obtained, and the invert ratio of 1,3-propanediol makes the object 96.0% was 32.9g (0.35 mols) and 69.5% of yield. Moreover, the content of 1 which carried out the byproduction, 3-dichloropropane, and the bis(3-chloropropyl) ether was 16.1% and 3.2% respectively. Subsequently, toluene 20.0g (40 % of the weight) was added using 50.0g of the water reaction mixture, and the organic layer including the ether object of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether which were put and carried out the byproduction after liquid separation was removed after churning. Consequently, the content of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether became 3.1% and 0.7% respectively. A detailed result is united and shown in a table 1.

[0025]Putting example 31 and 3-propanediol 152.3g (2.0 mols) into the 4 opening flask equipped with a reflux capacitor, a thermometer, and a magnetic churning child, attaching it to an oil bath, and agitating it, hydrogen chloride gas 88g (2.4 mols) was blown, and was made to react over 11 hours with the internal temperature of 93 degrees C - 96 degrees C. Consequently, the 3-chloro-1-propanol which 239.5g of water reaction mixture is obtained, and it makes 90.3% of invert ratios of 1,3-propanediol and the object was 117.8g (1.25 mols) and 62.3% of yield. Moreover, the content of 1 which carried out the byproduction, 3-dichloropropane, and the bis(3-chloropropyl) ether was 17.6% and 1.6% respectively. Subsequently, toluene 46.1g (20.2 % of the weight) was added to 228.5g of obtained water reaction mixture, and the organic layer including the ether object of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether which were put and carried out the byproduction after liquid separation was removed after churning. Consequently, the content of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether became 7.8% and 0.7% respectively. When this water reaction mixture was distilled by the top temperature of 57 degrees C / 10Torr, the high grade 3-chloro-1-propanol made into the object was obtained at 92.3g (0.98 mols) and 51.0% (99.0% [of purity], 1, 3-dichloropropane 0%, and bis(3-chloropropyl) ether 0.7%) of yield. A detailed result is united and shown in a table 1.

[0026]Putting example 41 and 3-propanediol 266.4g (3.5 mols) into the 4 opening flask equipped with a reflux capacitor, a thermometer, and a magnetic churning child, attaching it to an oil bath, and agitating it, hydrogen chloride gas 153g (4.2 mols) was blown, and was made to react over 17 hours with the internal temperature of 93 degrees C - 98 degrees C. Consequently, the 3-chloro-1-propanol which 413.8g of water reaction mixture is obtained, and it makes 93.9% of invert

ratios of 1,3-propanediol and the object was 200.5g (2.13 mols) and 60.6% of yield. Moreover, the content of 1 which carried out the byproduction, 3-dichloropropane, and the bis(3-chloropropyl) ether was 22.2% and 2.4% respectively. Subsequently, toluene 1.0g (40 % of the weight) was added using 2.5g of the water reaction mixture, and the organic layer including the ether object of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether which were put and carried out the byproduction after liquid separation was removed after churning. Consequently, the content of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether became 4.2% and 0.5% respectively. A detailed result is united and shown in a table 1.

[0027]Using 2.5g of water reaction mixture obtained like example 5 example 2, heptane 1.0g (40 % of the weight) was added, and the organic layer including the ether object of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether which were put and carried out the byproduction after liquid separation was removed after churning. Consequently, the content of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether became 5.3% and 0.7% respectively. A detailed result is united and shown in a table 1.

[0028]Using 2.5g of water reaction mixture obtained like example 6 example 2, chlorobenzene 1.0g (40 % of the weight) was added, and the organic layer including the ether object of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether which were put and carried out the byproduction after liquid separation was removed after churning. Consequently, the content of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether became 5.5% and 0.7% respectively. A detailed result is united and shown in a table 1.

[0029]Example 1l of comparison and 3-propanediol 266.4g (3.5 mols) is put into the 4 opening flask equipped with a reflux capacitor, a thermometer, and a magnetic churning child, and it attaches to an oil bath, and keeping the temperature of an oil bath at 165 degrees C, and agitating it, hydrogen chloride gas 134g (3.7 mols) was blown, and was made to react over 16.0 hours. Although generation of water was seen as the reaction progressed, it completed during the reaction, without performing clearance of the water out of a system. Consequently, the internal temperature fell gradually with generation of water from 160 degrees C, and the internal temperature fell even at 102 degrees C eventually. Moreover, the presentation of the obtained water reaction mixture was as follows. The 3-chloro-1-propanol which the content of 1 which carried out the byproduction, 3-dichloropropane, and the bis(3-chloropropyl) ether is 12.6% and 7.4% respectively, and is made into the object 92.7% of invert ratios of 1,3-propanediol was 135.8g (0.95 mols) and 41.7% of yield. Subsequently, toluene 152.0g (40 % of the weight) was added using 380g of the water reaction mixture, and the organic layer including the ether object of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether which were put and carried out the byproduction after liquid separation was removed after churning. Consequently, the content of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether became 1.8% and 1.6% respectively. The presentation after the yield in each process, the invert ratio of a raw material, the selectivity of a reaction, and processing at each process (the rate of the area by GC measurement shows) is shown in a table 2.

[0030]
[A table 2]

比較例	工程	工程収率 (mol%)	転化率 (%)	選択率 (%)	反応組成（GC area%）					
					CPO	DCP	2量体1	PDOL	2量体2	その他
1	反応	41.7	92.7	51.8	48.0	12.6	7.4	7.3	13.1	11.6
	抽出	91.8	—	—	52.1	1.8	1.6	14.5	16.2	13.8
2	反応	18.5	35.6	52.4	22.2	0.6	0	64.4	0.2	12.6
	抽出	87.7	—	—	22.0	0	0	65.9	0.2	12.8
3	反応	80.9	90.6	71.0	64.3	16.7	1.9	9.4	3.2	4.5
	蒸留	14.4	—	—	99.1	0	0.8	0	0	0.1

DCP：1，3－ジクロロプロパン
CPO：3－クロロ－1－プロパノール
PDOL：1，3－プロパンジオール
2量体1：ビス（3－クロロプロピル）エーテル
2量体2：3－クロロプロピル－3－ヒドロキシプロピルエーテル

[0031]Putting example 21 of comparison, and 3-propanediol 152.3g (2.0 mols) into the 4 opening flask equipped with a reflux capacitor, a thermometer, and a magnetic churning child, attaching it to an oil bath, and agitating it, hydrogen chloride gas 77g (2.1 mols) was blown, and was made to react over 13.4 hours with the internal temperature of 55 degrees C. Consequently, 212.0g of water reaction mixture was obtained. Moreover, although the content of the problem impurity 1 in water reaction mixture, 3-dichloropropane, and the bis(3-chloropropyl) ether was respectively as low as 0.6% and 0%, the 1,3-propanediol whose 3-chloro-1-propanol made into the object 34.9g (0.37 mols), 18.5% of yield, and the invert ratio of 1,3-propanediol are 35.6%, and is a start compound remained 64.4%. Subsequently, toluene 80.0g (40 % of the weight) was added using 200.0g of the water reaction mixture, and the organic layer including the ether object of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether which were put and carried out the byproduction after liquid separation was removed after churning. Consequently, the content of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether became 0% and 0% respectively. A detailed result is shown in a table 2.

[0032]Putting example 31 of comparison, and 3-propanediol 152.2g (2.0 mols) into the 4 opening flask equipped with a reflux capacitor, a thermometer, and a magnetic churning child, attaching it to an oil bath, and agitating it, hydrogen chloride gas 88g (2.4 mols) was blown, and was made to react over 11 hours with the internal temperature of 93 degrees C - 95 degrees C. Consequently, the 3-chloro-1-propanol which 234.15g of water reaction mixture is obtained, and it makes 90.6% of invert ratios of 1,3-propanediol and the object was 115.1g (1.22 mols) and 60.9% of yield. Moreover, the content of 1 which carried out the byproduction, 3-dichloropropane, and the bis(3-chloropropyl) ether was 16.7% and 1.9% respectively. Subsequently, the place which distilled 223.4g of water reaction mixture by the top temperature of 50 degrees C / 9Torr as it was, without a hydrophobic organic solvent performing extract clearance for the impurity in water reaction mixture, Although distillation separation with the bis(3-chloropropyl) ether was difficult and the high grade 3-chloro-1-propanol made into the object was obtained at bis(3-chloropropyl) ether 0.8% 16.6g (0.18 mols), 99.1% of purity, 1, and 3-dichloropropane 0%Yield was 8.8%. A detailed result is united and shown in a table 2.

[0033]When the above examples 1-6 and examples 1-3 of a comparison were compared, it turned out that an impurity is removable by extracting reaction mixture with a hydrophobic organic solvent after a chlorination reaction like an example, and the purity can improve by distilling this further while being high yield and obtaining the 3-chloro-1-propanol of a high grade. On the other hand, it turns out that it cannot do well in that the 3-chloro-1-propanol of a high grade is not obtained, and distilling unless a hydrophobic organic solvent extracts reaction mixture so that the example of a comparison may see, but the yield worsens.

[0034]The organic layer including the ether object of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether which put 0g, 0.25g (10 % of the weight), 0.5g (20 % of the weight), and 1.0g (40 % of the weight) after churning moreover, and carried out the byproduction of the amount of toluene which uses for an extract the water reaction mixture obtained like example 7 example 4 using 2.5g after liquid separation was removed. Consequently, the content of the bis(3-chloropropyl) ether became 2.00%, 1.57%, 0.90%, and 0.51%, respectively.

[0035]This shows that the elimination factor of ether objects, such as extractability, 1 [i.e.,], and 3-dichloropropane and the bis(3-chloropropyl) ether, becomes high according to the amount which adds the extract effectiveness of toluene.

[0036]The organic layer including the ether object of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether which put 0g, 0.125g (5 % of the weight), 0.25g (10

% of the weight), 0.5g (20 % of the weight), and 1.0g (40 % of the weight) after churning moreover, and carried out the byproduction of the amount of heptanes which uses for an extract the water reaction mixture obtained like example 8 example 5 using 2.5g after liquid separation was removed. Consequently, the content of the bis(3-chloropropyl) ether became 2.00%, 1.44%, 1.22%, 0.98%, and 0.72%, respectively.

[0037]This shows that the elimination factor of ether objects, such as extractability, 1 [i.e.,], and 3-dichloropropane and the bis(3-chloropropyl) ether, becomes high according to the amount which adds the extract effectiveness of a heptane.

[0038]The organic layer including the ether object of 1 and 3-dichloropropane and the bis(3-chloropropyl) ether which put 0g, 0.5g (20 % of the weight), and 1.0g (40 % of the weight) after churning moreover, and carried out the byproduction of the amount of chlorobenzenes which uses for an extract the water reaction mixture obtained like example 9 example 6 using 2.5g after liquid separation was removed. Consequently, the content of the bis(3-chloropropyl) ether became 2.00%, 1.21%, and 0.66%, respectively.

[0039]This shows that the elimination factor of ether objects, such as extractability, 1 [i.e.,], and 3-dichloropropane and the bis(3-chloropropyl) ether, becomes high according to the amount which adds the extract effectiveness of a chlorobenzene.

[0040]

[Effect of the Invention]Since the high grade 3-chloro-1-propanol which is an important compound industrially can be easily obtained from the 1,3-propanediol which is a cheap start compound efficiently as useful raw materials, such as a remedy, agricultural chemicals, and a polymer, according to the approach of this invention, this manufacturing method is useful as the industrial manufacture approach of high grade 3-chloro-1-propanol.